Photofragmentation of Small Molecules Following Excitation at Deep-Core Levels

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The relaxation dynamics of HCl, DCl, H_2S, and D_2S following photoexcitation in the vicinity of the Cl and S K-shell thresholds ($\sim$2.8 keV for Cl, $\sim$2.5 keV for S) were studied by means of ion time-flight mass spectroscopy using light from B.L. 9.3.1. In all cases, a significant amount of neutral dissociation of hydrogen was found to occur on resonance, as well as the onset of pre-edge core-shell photoexcitation.

The data presented here were collected in two different modes. In the "singles" mode, time-of-flight spectra are collected with only one or two electron bunches circulating in the storage ring. The start pulse for the timing circuit is provided by the detection of an individual ion, while the ring timing pulse, produced by the periodic pulsing of the SR (328 ns for ALS 2-bunch), provides the stop signal. In the PIPICO mode of operation, two ions from the same molecule provide the start and stop signals for the timing circuit (in this case, H^+ provides the start, and Cl^{n+} or S^{n+} provide the stop). Thus the difference in flight time between the two ions is measured, and the operation mode of the storage ring is irrelevant. These measurements inherently discriminate against decay processes where the molecule does not dissociate, or where the molecule dissociates but one of the fragments is neutral. Fig. 1 shows spectra taken on resonance for HCl, and H_2S. The most notable feature of these spectra is the high degree of

FIG. 1. TOF spectra of HCl and H_2S taken above the first resonance Two isotopes of chlorine and sulfur are visible.

ionization of the atoms (+6 for Cl, +5 for S), and the fact that fragmentation of the molecule happens following the majority of interactions, with less than 1% of the yield being the result of molecular ions. The data analysis procedure is essentially the same for both PIPICO and singles spectra. Spectra were taken at a number of photon energies in the Cl K-shell region. Peaks in these spectra were integrated in order to calculate fractional yields as a function of energy.

In the photon energy regime below the 1s$\rightarrow 6\sigma^*$ resonance gradual changes in the relative abundances of the different ionic states are visible in the average charge state for both the singles and PIPICO spectra (Fig. 2). We attribute this effect to pre-edge inner-shell ion-
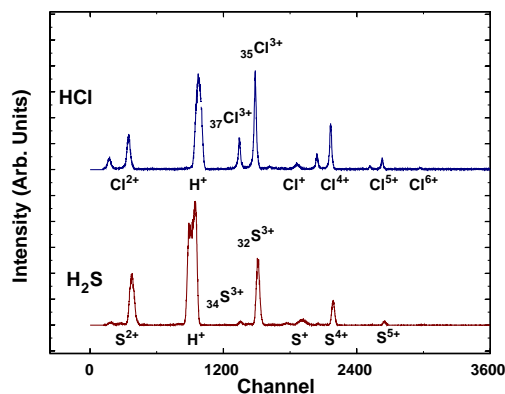
ization, where the photoelectron is excited to the Lorentzian profile of a continuum state. Previous studies have observed the onset of this effect at tens of eV below the 1s→4s resonance for Ar and for more than 10 eV below the first sulfur K-edge resonance in OCS and CS_2. While in this study, the data does not allow for an accurate determination of the onset of pre-edge ionization, it can be safely said that it occurs at energies more than 5 eV below the 1s→ $6\sigma^*$ resonance.
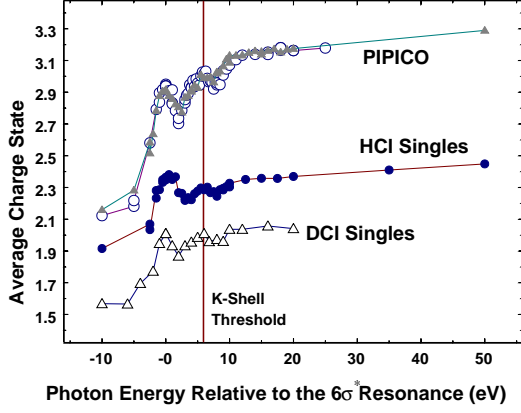

FIG. 2. Average charge state for HCl and DCl singles and PIPICO spectra. Circles represent the HCl data, triangles represent the DCl data.
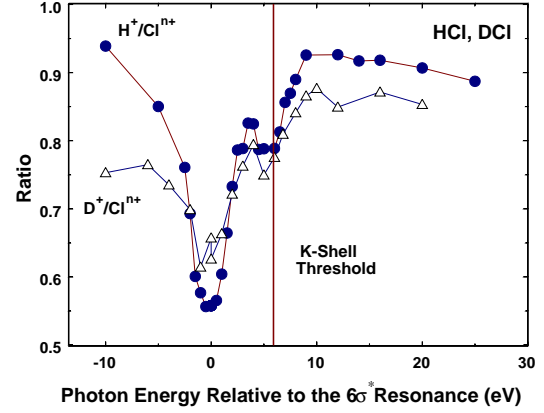

FIG. 3. Ratio of hydrogen or deuterium ions detected to the sum of all chlorine ions detected in singles mode.
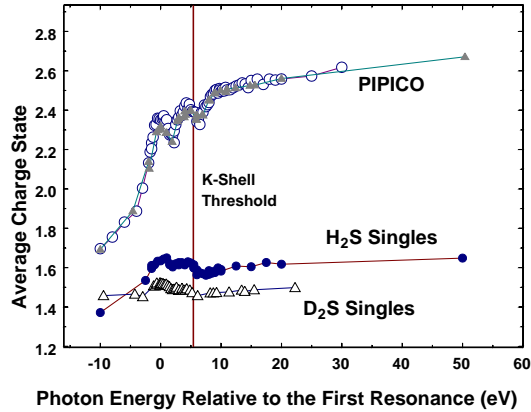

FIG. 4. Average charge state for H_2S and D_2S singles and PIPICO spectra. Circles represent the H_2S data, triangles represent the D_2S data.
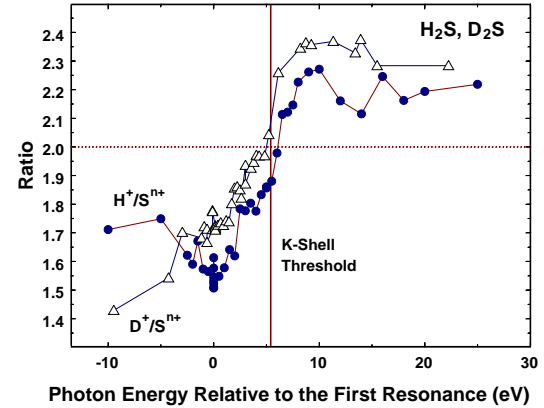

FIG. 5. Ratio of hydrogen or deuterium ions detected to the sum of all sulfur ions detected in singles mode.

Fig. 3 shows the ratio of the H^+ yield to the sum of the yields for all Cl charge states. The most notable feature in this data is the drop in the hydrogen to chlorine ratio of as much as 40% for HCl, and 20% for DCl on resonance. Although the DCl molecule undergoes the same decay transitions as the HCl molecule, the amount of neutral hydrogen produced is less by almost a factor of two. This is easily explained by the fact that the heavier deuterium does not escape the attractive potential of the Cl^{+n} ion as quickly as the hydrogen atom, and it is thus more difficult for the deuterium atom to carry away an electron in the presence of the more electronegative chlorine ion.

Discussion of the results for H_2S and D_2S can, for the most part, parallel the discussion for HCl and DCl. Trends in the the average charge state of the S^{n+} ion (Fig. 4) indicate

the onset of pre-edge inner-shell ionization, and, again there is a dip in the ratio of H^+/S^{n+} on resonance. Both of these effects are analogous to those observed in HCl. However in the energy regime below resonance, the ratio of D^+/S^{n+} is significantly lower than on resonance values. This can be attributed to a higher production of the molecular ion below resonance. Because the ratio is lower than that for H_2S, it seems likely that the trends are a result of a kinematic effect where the heavier deuterium is not able to escape the sulfur ion as easily as the hydrogen.

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